$$T_{c1} = 2\int_0^{x_m} dx \left(\frac{m}{2[E - V(x)]}\right)^{1/2}.$$

Since $V(x)$ is not of simple form we cannot calculate this integral exactly by other than numerical means. However, we can find functions $V_u(x)$ and $V_l(x)$ which are upper (u) and lower (l) bounds for $V(x)$ and permit exact integration of T_{c1}:

$$V_u(x) > V(x) > V_l(x),$$

$$V_l(x) \equiv -e^2/4x,$$

$$V_u(x) \equiv V(x_m) - V'(x_m)(x_m - x)$$

$$= E - V'(x_m)(x_m - x),$$

where the prime denotes differentiation. The resulting upper and lower bounds for the period are, respectively,

$$T_{c1}^{(u)} = \left(\frac{2mx_m}{V'(x_m)}\right)^{1/2},$$

$$T_{c1}^{(l)} = \left[\frac{me^4}{32|E|^3}\right]^{1/2} [(u+u^2)^{1/2} - \ln((1+u)^{1/2} + u^{1/2})], \tag{B3}$$

$$u = 4|E|x_m/e^2.$$

Comparison of these quantities shows that $T_{c1}^{(u)}$ is a factor of 5–10 larger than $T_{c1}^{(l)}$. For convenience we will take the actual value to be

$$T_{c1} \approx \tfrac{1}{2} T_{c1}^{(u)}. \tag{B4}$$

This imprecision is not significant for an order-of-magnitude estimate since T_{c1} is only a preexpotential factor.

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[1] J. Jortner, N. R. Kestner, and M. H. Cohen, J. Chem. Phys. 43, 2614 (1965); B. E. Springett, J. Jortner, and M. H. Cohen, *ibid.* 48, 2720 (1968).

[2] W. T. Sommer, Phys. Rev. Letters 12, 271 (1964); M. A. Woolf and G. W. Rayfield, *ibid.* 15, 235 (1965); B. Halpern and R. Gomer, J. Chem. Phys. 51, 1031 (1969).

[3] M. W. Cole and M. H. Cohen, Phys. Rev. Letters 23, 1238 (1969).

[4] M. W. Cole, Phys. Rev. B 2, 4239 (1970), henceforth referred to as I.

[5] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, London, 1960), p. 40.

[6] W. A. Harrison, Phys. Rev. 123, 85 (1961).

[7] D. J. BenDaniel and C. B. Duke, Phys. Rev. 152, 683 (1966).

[8] We do not include the contribution associated with the vacuum-vapor interface, which is important only within a few angstroms of $x = 0$. See Sec. III and Appendix B for the actual variation of the potential in the dielectric.

[9] J. R. Oppenheimer, Phys. Rev. 31, 66 (1928); J. Bardeen, Phys. Rev. Letters 6, 57 (1961); E. C. Kemble, *Fundamental Principles of Quantum Mechanics* (Dover, New York, 1958), Sec. 31.

[10] C. B. Duke, *Tunneling in Solids* (Academic, New York, 1969), Secs. 1, 4, 6.

[11] D. R. Hartree, *Numerical Analysis* (Oxford U. P., London, 1958), p. 126.

[12] E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge U. P., London, 1963), Sec. 16.

[13] D. Newns [J. Chem. Phys. 50, 4572 (1969)] has used a similar method.

[14] The classical solution is not reliable within a few angstroms of either interface. Since Eq. (B1) is the solution for the infinite dielectric problem, by using it we neglect the influence of the vapor, a satisfactory approximation. Neither of these oversimplifications affects the results significantly.

[15] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, London, 1958), Sec. 50.

[16] In the following we omit the parameter t from $V(x, t)$.

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Infrared Absorption of Small NaCl Crystals[*]

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Results of recent measurements of the infrared absorption of small NaCl crystals are compared with calculated absorption spectra.

The infrared absorption in the reststrahlen region of small crystals of NaCl has recently been measured by Martin.[1] The samples used were rectangular in shape, with two of their sides of length 10 μ and the third one shorter. (This size represents, however, only the average over a wide experimental size distribution.[2]) The crystallites were embedded in polyethylene and were well separated. The spectra observed at 7 and 290 °K are shown in Fig. 1.

As noted by Martin,[1] the highest-frequency (frequency here measured in wave-number units) secondary minima (at about 216 cm^{-1} for 290 °K and at about 232 cm^{-1} for 7 °K) are probably due to two-

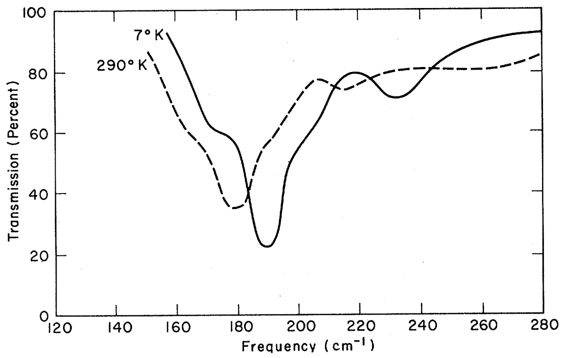

FIG. 1. Infrared transmission through small crystals of NaCl (after Martin, Ref. 1).

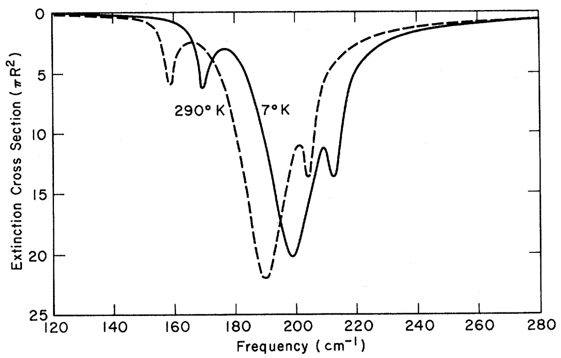

FIG. 2. Calculated extinction cross section of a NaCl sphere of radius 4 μ embedded in polyethylene.

phonon absorption. The remaining first-order structure, i.e., the strong main minimum with its two shoulders at the low- and the high-frequency sides should, in principle, be explicable in terms of the recently developed theories of the size and shape dependence of the optical phonon frequencies.[3–5] However, the application of the general theory to rectangular crystals involves calculational difficulties which are not yet overcome. Therefore only a comparison with the calculated absorption of spherical samples can be attempted. Martin in fact compared the experimental results with a previously calculated spectrum of a NaCl sphere of diameter 20 μ in air[4] and found no agreement. This discrepancy is not surprising since the experimental conditions (particle size and surrounding medium) were different from those to which the calculation referred.

We present here the calculated spectrum for NaCl spheres in polyethylene surroundings (the dielectric constant of which is equal to 2.3). We have found that spheres of diameter 8 μ give the best agreement with the experimental three-peak structure (Fig. 2). For this calculation the frequency-dependent dielectric constant

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 - (\omega^2/\omega_T^2) - i\gamma(\omega/\omega_T)}$$

has to be given. For the low- and high-frequency dielectric constants, the transverse frequency, and the damping constant, the following experimental values have been used[1,6]: $\epsilon_0(7\,°\mathrm{K}) = 5.46$, $\epsilon_0(290\,°\mathrm{K}) = 5.90$, $\epsilon_\infty(7\,°\mathrm{K}) = 2.351$, $\epsilon_\infty(290\,°\mathrm{K}) = 2.329$, $\omega_T(7\,°\mathrm{K}) = 175\ \mathrm{cm}^{-1}$, $\omega_T(290\,°\mathrm{K}) = 164\ \mathrm{cm}^{-1}$, $\gamma = 0.02$. The method of calculation has been described in detail in Ref. 7. The calculated quantity is the extinction cross section of one sphere rather than the total absorption. The latter cannot be calculated unless the number of crystallites per unit volume is given.

The discrepancies between the calculated and the observed absorption frequencies are 10 cm^{-1} at most, which is as good as can be expected, considering the different geometries involved. The three absorption lines are identified as follows. The secondary line slightly below ω_T is due to bulk mode absorption, whereas the main minimum, as well as the other secondary line, are due to surface mode absorption. The fact that the measured secondary lines are not as sharp as the calculated ones is probably a consequence of the wide size variation of the individual particles about the average size.

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[1] T. P. Martin, Phys. Rev. B 1, 3480 (1970).

[2] T. P. Martin (private communication).

[3] R. Englman and R. Ruppin, J. Phys. C 1, 614 (1968).

[4] R. Ruppin and R. Englman, J. Phys. C 1, 630 (1968).

[5] R. Fuchs and K. L. Kliever, J. Opt. Soc. Am. 58, 319 (1968).

[6] R. P. Lowndes and D. H. Martin, Proc. Roy. Soc. (London) A308, 473 (1969).

[7] R. Ruppin and R. Englman, Rept. Progr. Phys. 33, 149 (1970).